

THE EFFECTS OF FUEL-BOUND CHLORINE AND ALKALI ON CORROSION INITIATION

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ABSTRACT

This investigation explores the effects of fuel-bound chlorine and alkali metals on the initial phases of metal corrosion under conditions typical of superheaters and reheaters in electric power generating boilers. Experiments were conducted with a variety of fuels in an entrained-flow, pilot-scale combustor that simulates conditions found in commercial-scale, pulverized-coal-fired boilers. Temperature-regulated probes simulated superheater tubes and were sized to reproduce similar mechanisms of deposition as are found in commercial systems. Fuels examined include coals with a wide range of chlorine concentrations, biomass fuels, and coals blended with chlorine-containing biomass fuels. Scanning electron micrographs reveal regions of the interfaces of some such probes that show evidence of chloride condensation and subsequent conversion to sulfates. This chemical conversion releases chlorine-containing gases that can facilitate the corrosion of the surface without being consumed. Hypothesized mechanisms for this corrosion have been presented in the literature and are reviewed. The extent to which chlorine-containing materials accumulate on surfaces and subsequently sulfate is shown to depend strongly on the mechanisms of ash deposition and on surface temperature. Interactions between alkali and other ash constituents are shown to effect the extent of alkali deposition and the amount of sulfation. Implications for combustion of chlorinated fuels are discussed.

INTRODUCTION

One of the primary economic drivers of this investigation is the determination of the level of chlorine in coal that can be allowed before corrosion of heat transfer surfaces becomes intolerable and how this level may vary among coals of similar properties but from different seams. In particular, authors have cited anecdotal evidence that coals from the Illinois region do not cause corrosion problems in boilers to the extent that UK coals with similar chlorine levels do. The UK has a great many chlorinated coals whereas the most commercially significant chlorinated coal in the US derive from the Herron Basin, largely within Illinois, and represent a fairly small fraction of the overall US coal market. Operational practices relative to chlorine-induced corrosion rely heavily on UK recommendations, where the greatest experience lies. Generally, these practices suggest not firing coals with greater than 0.3% chlorine unless materials and operations are specifically altered to deal with potential corrosion problems associated with high-chlorine coals.

There have been no direct comparisons of the corrosion behaviors of UK and US coals in the same utility-scale boiler under the same operating conditions. Since such comparisons are both unlikely to occur and are subject to large uncertainty due to the nature of commercial-scale operation, this investigation was commissioned. The objective of this work is to establish fundamental relationships among operating conditions, fuel properties, and corrosion mechanisms that could be used to establish the corrosion potential of fuels.

Sandia National Laboratories is engaged in a series of investigations regarding the role of chlorine in corrosion in power plants. These investigations focus on deposit formation and initiation of corrosion processes. Chlorine-based corrosion is often associated with alkali metals, and corrosion in general is often aggravated by alkali metals with or without chlorine present. The purpose of this investigation is to establish which corrosion-related species are most likely to form in the gas-phase and on surfaces under typical combustion conditions and to demonstrate how fuel properties influence their formation. This information leads to a postulated mechanism for chlorine-related corrosion and distinguishing characteristics among fuels that may indicate their corrosion potential.

THERMODYNAMIC STABILITY

Early work on this subject indicated that there may be differences in the rates of release of chlorine depending on the origin of the coal. Specifically, coals from the UK were observed to release chlorine slightly earlier in their combustion histories than were US coals of otherwise similar properties. There was some speculation that this could lead to differing corrosion rates or mechanisms. However, in all cases essentially all of the chlorine was released well before the coals completed

¹ Work completed while visiting Sandia National Laboratories, Livermore, CA, from the Technical University of Denmark, Copenhagen.

combustion. Therefore, all of the chlorine would be in the gas phase long before entering the convection passes of commercial boilers, where corrosion is typically of greatest concern. We view it as unlikely that differences in these early release mechanisms could significantly alter the corrosion rates that occur far downstream from where the differences are observed. However, there may be differences in the coals that lead to differing amounts of alkali being released. These may be more closely related to modes of alkali occurrence than to release rates and mechanisms of chlorine. Alkali metals are clearly implicated in high-temperature corrosion and their most stable gas-phase form is as chlorides at furnace exit gas temperatures.

Table 1 Elemental composition on which equilibrium calculations are based representing an oxidizing, moist environment typical of lower-furnace regions in many coal-fired boilers. There is excess oxygen, carbon and hydrogen for formation of alkali carbonates and hydroxides, but insufficient sulfur or chlorine to react with all of the alkali to form sulfates or chlorides.

Element	Molar Ratio Element / Total Alkali
C	202
H	850
O	1593
N	5848
S	0.125
CL	0.375
Alkali (Na or K)	1

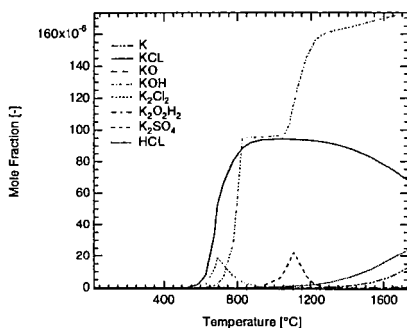


Figure 1 Equilibrium species concentrations for the major potassium-containing, gas-phase species present under typical coal combustion conditions. Compare with condensed-phase behavior illustrated in Figure 2.

Figure 1 through Figure 4 illustrate equilibrium predictions for the major alkali-containing gas- and condensed-phase species as a function of temperature. As illustrated, chlorine and alkali behavior are coupled and this coupling explains some aspects of how ash deposit structure develops. All of the calculations are performed under conditions representative of furnace regions where chlorine is released and char oxidation begins. The molar ratios of each of the atoms relative to the alkali-containing species are indicated in Table 1. In general, the oxygen and water mole concentrations in the equilibrium products are about 10%. The molar ratios allow for complete conversion of alkali to carbonates or hydroxides, but are insufficient to allow complete conversion to either sulfates or chlorides.

Chlorides represent among the most stable alkali-bearing species in the gas phase. Chlorine is shown to have a strong affinity for alkali metal in the temperature ranges of interest to convection pass entrances. In many cases, the amount of alkali vaporized during combustion is determined more by the amount of chlorine available to form stable vapors than by the amount of alkali in the fuel ¹. Figure 1 illustrates predicted equilibrium concentrations of gas-phase, potassium-containing species under typical coal-combustion conditions. Condensed-phase results are illustrated in Figure 2. Gas-phase sulfate is seen to play a relatively minor role in potassium equilibrium chemistry. Peak sulfate concentrations represent about 10% of the total gas-phase potassium and occur over a narrow temperature range at about 1100 °C. At lower temperatures, potassium sulfate vapor condenses to form liquid or solid sulfate. At higher temperatures, it decomposes. Thermodynamic predictions of sodium-bearing species are very similar to those of potassium and are illustrated separately in Figure 3 and Figure 4.

The dominant gas-phase, alkali-bearing species at flame temperatures (>1400 °C) is alkali hydroxide, followed by the chloride. In the absence of significant chlorine for reaction, only the hydroxide is present. As temperatures cool to convection-pass values (<1000 °C), hydroxides convert to chlorides, the only alkali-bearing species in significant quantities at lower temperatures. Sulfates are notable by their absence in the gas phase.

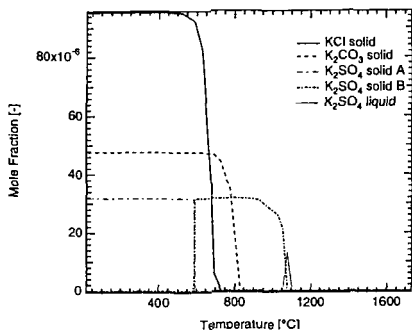


Figure 2 Condensed-phase equilibrium behavior of potassium-containing species. Compare with gas-phase behavior illustrated in Figure 1.

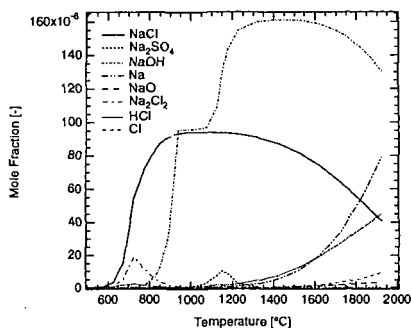


Figure 3 Equilibrium species concentrations for the major sodium-containing, gas-phase species present under typical coal-combustion conditions.

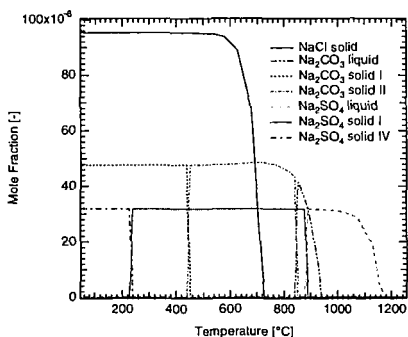


Figure 4 Equilibrium species concentrations for the major sodium-containing, condensed-phase species present under typical coal-combustion conditions.

The condensed-phase behavior of alkali-containing compounds is illustrated in Figure 2 and Figure 4 as a function of temperature. Many coals have more sulfur than the stoichiometric amount required for reaction with all of the available alkali. In addition, an ash deposit on a surface interacts with a continuous gas stream, providing a continuous source of sulfur. Often, the rate of accumulation of alkali in the deposit is slow compared to the rate of diffusion of sulfur from the bulk gas stream to the deposit surface. Under these conditions, the deposit has opportunity to react with a much larger amount of sulfur than the elemental composition of the fuel may suggest. However, these calculations include less sulfur than is required to react with available alkali to illustrate the relative stability of chlorides and sulfates in the condensed phase. Sulfates are the most stable of the condensed-phase alkali species at temperatures indicative of heat transfer surfaces and deposits (1200 °C and less).

Equilibrium predictions show that the dominant condensed-phase species at the highest temperatures are sulfates, followed by carbonates and chlorides as temperature decreases. Historical Multifuel Combustor data and field data have shown that sulfates, carbonates, and chlorides are commonly found on heat transfer surfaces when combusting fuels that contain none of these compounds; i.e. these species are formed in the furnace and not simply transported with the ash to the surface. Sulfates are invariably found in highest concentrations and can be seen to form with time on the surface². Carbonates and chlorides are less commonly found but have been observed in deposits from highly chlorinated coals and under reducing conditions.

MODE OF OCCURRENCE

Essentially all of the chlorine in fuels is available for reaction in the gas phase. The same is not true of the alkali. A large fraction of the alkali material occurs in a mode that is either thermodynamically stable or physically constrained such that it is not available for interaction with other compounds. An extraction technique known as chemical fractionation is used to distinguish between these modes of occurrence of different inorganic species in coal, including the alkalis. Specifically, the technique is used to determine the relative availabilities of inorganic material for vaporization or other release processes during combustion. The technique involves extracting material from a sample of coal using increasingly aggressive reagents and monitoring the fraction of inorganics extracted at each step. We typically separate inorganics into four groups:

- (1) water soluble materials such as halides, some salts, and some chemisorbed or otherwise lightly

bound inorganics; (2) ion exchangeable materials such as ions of salts formed from carboxyl and hydroxyl groups in the coal; (3) acid soluble materials such as carbonates and sulfates; and (4) residual materials such as clays and most oxides (silica, titania, etc.).

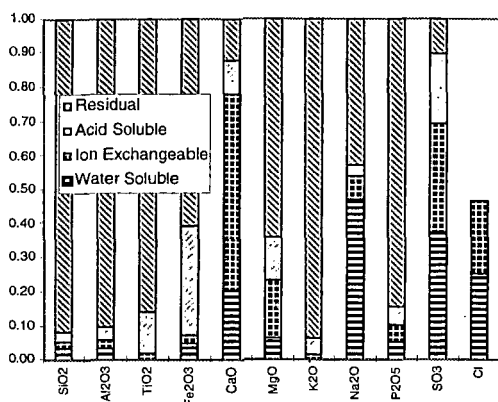


Figure 5 Chemical fractionation results for the UK coal indicating the major modes of occurrence for the inorganic components. Compare with Figure 6.

Results of this procedure are available for representative UK and a US coals with similar chlorine contents. The results indicate that there is approximately 50% more sodium available from the UK coal for participation in the corrosion-inducing reactions indicated above than there is for the US coal. However, the difference arises from the total sodium content and not from a large difference in the mode of occurrence of the sodium in the fuels. Figure 5 illustrates the results for the UK coal. The fraction of total mass is illustrated for each of the major elements in coal. Sodium is of primary interest for corrosion for these fuels. Sodium occurring in mobile forms is more likely to vaporize during combustion than sodium in

the form of clay or other stable compounds. The mobile forms of sodium include the water soluble and ion exchangeable components. The sum of these two forms represents 54% of the sodium in the UK coal and 66% in the Rend Lake coal. This difference is larger than the inherent error in making these measurements ($\pm 3\%$), but is probably not significantly larger than the fluctuations in coal properties as delivered from the mine. We find no indication that the modes of occurrence of sodium or chlorine in these two samples of fuels would produce significantly different corrosion results. There are large variations in the mode of occurrence of sodium in coal, and other fuels may show different tendencies. We do anticipate the UK coal would be more corrosive than the US coal in this case, but only because it has a higher overall sodium content. The modes of occurrence of sodium in the two fuels are similar.

Table 2 Chemical fractionation results for the UK coal indicating the major modes of occurrence for the inorganic components on a % dry fuel basis. Compare with Table 3.

	SiO ₂	Al ₂ O ₃	TiO ₂	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	P ₂ O ₅	SO ₃	Cl
Water Soluble	0.251	0.135	0.000	0.046	0.053	0.014	0.000	0.133	0.001	0.086	0.017
Ion Exchangeable	0.179	0.085	0.002	0.025	0.152	0.040	0.008	0.020	0.001	0.073	0.014
Acid Soluble	0.213	0.159	0.016	0.299	0.026	0.031	0.025	0.009	0.001	0.048	
Residual	7.457	3.553	0.108	0.577	0.032	0.152	0.506	0.121	0.022	0.024	

Table 3 Chemical fractionation results for the Illinois coal indicating the major modes of occurrence for the inorganic components on a % dry fuel basis. Compare with Table 2.

	SiO ₂	Al ₂ O ₃	TiO ₂	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	P ₂ O ₅	SO ₃	Cl
Water Soluble	0.042	0.014	0.000	0.087	0.098	0.018	0.005	0.090	0.001	0.056	0.008
Ion Exchangeable	0.220	0.107	0.006	0.030	0.153	0.049	0.011	0.001	0.002	0.093	0.007
Acid Soluble	0.067	0.063	0.006	0.208	0.008	0.008	0.007	0.004	0.001	0.024	
Residual	3.497	1.614	0.080	0.814	0.038	0.064	0.166	0.042	0.015	0.027	

THE ROLES OF CHLORINE AND ALKALI IN CORROSION

On the basis of these data we postulate the following relationships among operating conditions, boiler design, and fuel properties that impact corrosion. The three fuel properties that most significantly impact rates of corrosion are sulfur, available alkali, and chlorine contents. Corrosion is

strongly influenced by the presence of alkali on the surface of the deposit. This alkali is generally sulfated on the surface, but it appears that the sulfate represents a reaction product from the gas phase and is not, in general, directly deposited. Chlorine enhances corrosion by at least two mechanisms. First, increased chlorine concentrations lead to increased alkali-containing vapors in combustion gases as chlorides are among the most stable alkali-laden species under most combustion conditions. Increased gas-phase alkali concentrations lead to increased rates of alkali deposition on surfaces. Secondly, if the alkali chlorides from the gas phase convert to alkali sulfates on or near heat transfer surfaces, the chlorinated product of the reaction will be concentrated near the heat transfer surface. Chlorine is known to enhance metal corrosion rates significantly under typical superheater conditions. The rate of alkali vaporization and subsequent sulfation can be limited by chlorine, alkali, or sulfur contents. If it is limited by sulfur content, we would expect to see chlorides on the surfaces of heat transfer equipment. If it is limited by chlorine content or alkali content, chloride content on the surface would be very low even though chlorine plays an important role in both transport of alkali to the surface and corrosion of the metal.

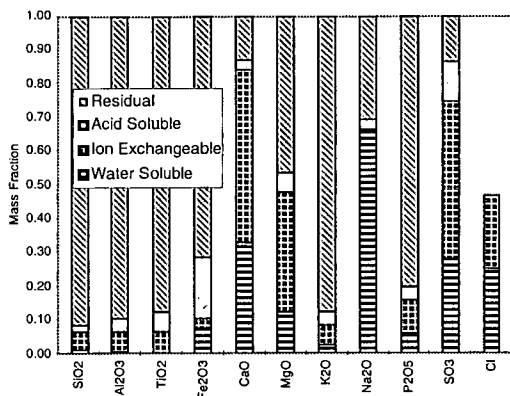


Figure 6 Chemical fractionation results for the Illinois coal indicating the major modes of occurrence for the inorganic components. Compare with Figure 5.

In a series of investigations we have tested essentially all of the aspects of this conceptual model of chlorine-enhanced corrosion. Alkali vaporization rates increase with increased fuel chlorine content. Alkali sulfates are commonly found concentrated at the metal-deposit interface of probes in the form of sulfates. Chlorides are found on the surface when chlorine levels are increased and sulfur contents are decreased. Figure 7 illustrates a layer of sodium and sulfur found on the surface of a simulated superheater tube during one such investigation. The duration of our tests is insufficient to determine whether these observations can be directly related to long-term corrosion rates, but they are consistent with investigations available in the

literature regarding long-term corrosion.

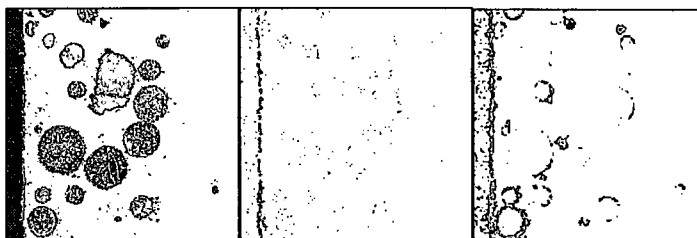


Figure 7 SEM image of cross-section of deposits formed on a probe in the Multifuel Combustor. The probe surface is on the left of each image. The images represent the probe surface with deposited particles (left), a sodium map (center), and a sulfur map (right).

REFERENCES

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